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# Thermochemical processing of meat and bone meal: A review

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ABSTRACT

Since the Bovine Spongiform Encephalopathy crisis, meat and bone meal (MBM) have been considered animal wastes. Nowadays, these animal residues are generally burnt in cement kilns and disposed of in landfills. However, several technologies are being developed in order to achieve energy valorisation of MBM by means of combustion, pyrolysis and gasification. These thermal treatments of MBM will reduce the environmental impact of landfill and, at the same time, take advantage of the MBM heating value (13–30 MJ/kg). The main results of research into combustion, pyrolysis and gasification of MBM show that the products could be used as fertilizer (solid product) and as fuel (gas and liquid products). The present work aims at reviewing the most significant studies about energy valorisation of MBM and the potential application of the products obtained in these thermochemical processes.



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## 1. Introduction and scope of the work

Meat and bone meal (MBM) is a by-product of rendering industries obtained after cooking mammal carcasses and eliminating fat, and finally drying and crushing. MBM has historically been used in cattle feed preparation. However, since the Bovine Spongiform Encephalopathy crisis (BSE), the addition of MBM as a protein rich product into cattle feed has been restricted in Europe [1]. Other countries such as Canada and the United States have also adopted laws preventing the use of specific risk materials in animal feed production [2].

In 2002, these animal wastes were classified in three different categories [3]. Category 1 is a high-risk material including the carcasses of animals infected or suspected to be infected with BSE, zoo and pet animals and specific risk materials. Category 2 is also high-risk material coming from animals which have died in farms. Category 3 is low-risk material from safe animals. MBM produced from Category 3 wastes are allowed to be used as pet food and agriculture fertilizers.

The quantities of MBM produced vary from country to country. For example, in the case of France more than 850,000 tons per year are generated [4], in Germany there is an estimated

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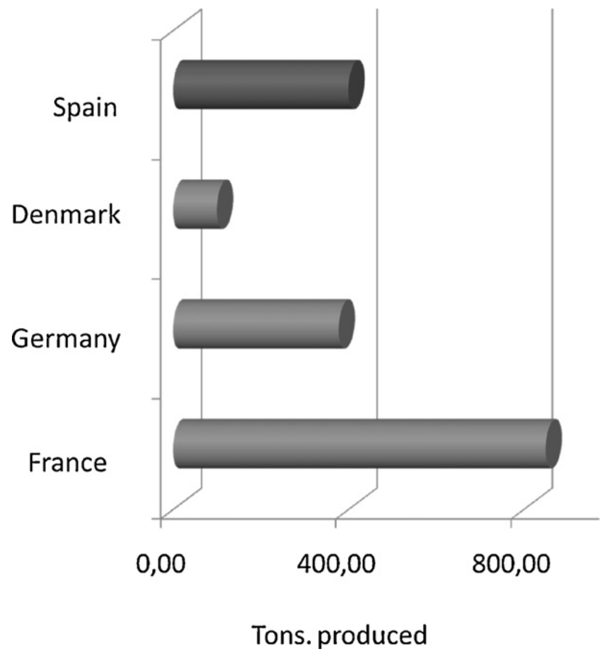



Fig. 1. MBM produced in some countries in Europe.

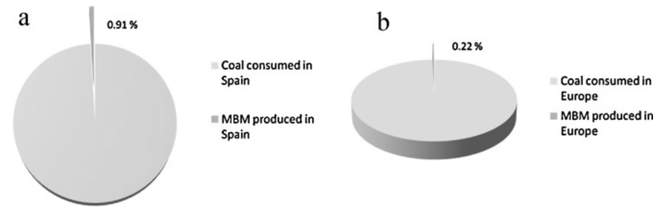



Fig. 2. Percentage of MBM compared to coal consumed in Spain (a) and in Europe (b).

production of 378 tons per year, in Switzerland the production is around 45,000 tons per year [5], 100,000 tons per year are produced in Denmark [6] and annually 400,000 tons are generated in Spain (see Fig. 1). More than 3.5 million tons per year of MBM are produced in total in the European Union [7].

One solution currently authorized by governments is its co-incineration in cement kilns. However, large amounts of MBM are also being disposed of in landfills due to the pressure of public opinion against incineration processes [8]. In Greece, animal manures are stocked in rural areas and outside animal farms, and create significant environmental problems such as underground water pollution, gas and odour emissions, vector attraction and general visual pollution [9].

Due to the medium-high heating value of this material, between 13 and 30 MJ/kg [2,4,5,8–17] alternative environmentally friendly thermochemical processes are being investigated by some research groups in order to better manage this residue. The use of MBM as a secondary fuel in a fluidised bed combustor has been the most frequently evaluated option [12–14,16–20]. Pyrolysis and gasification have been investigated to a lesser degree than co-combustion [2,4,8,15,17,21–25]. Given the chemical composition of MBM, some authors have analysed other alternatives such as the use of MBM as solid fertilizer [26] and even the biological treatment of MBM for $CH_4$ gas production by means of anaerobic digestion [27,28].

The use of MBM as a secondary fuel in thermochemical processes could result in a noticeable saving in Europe. For example, the amount of MBM produced in Spain during a year is 400,000 tons (as mentioned above). The total cost of disposing of MBM in landfills is 15.2 million euro (38 euro/ton) with an energetic waste of 8600 million MJ (21.5 MJ/kg). The coal consumed in thermal units in Spain is 44 million tons per year. MBM wastes could be burnt in thermal plants by replacing 0.91 wt.% of the total coal used in these plants (Fig. 2). Therefore, the cost of MBM land-filling could be reduced and the cost of coal (60 euro/ton) substituted by MBM could also be eliminated. Thus, more than 39 million of euro/year could be saved in Spain.

The amount of MBM produced in Europe is 3.5 million of tons/year (as mentioned above) and the coal used in thermal processes is 1380 million tons/year (Fig. 2). Thus, 0.22 wt.% of the coal used in Europe could be substituted by MBM wastes with the subsequent economical saving.

The scope of the present paper is to carry out a literature review of the most relevant works developed in the field of thermochemical treatments of MBM, focusing on the types of reactors used, the product yields and the uses of the products obtained from these treatments. The structure of the present work has been arranged in an attempt to provide the information with the greatest clarity as possible. Therefore, a summary of the papers mentioned is related at the beginning of each section and, afterwards, a more extensively discussion about the results from these works is provided.

## 2. Physical and chemical characterisation of meat and bone meal

MBM physical and/or chemical characterisation is performed before its use as raw material in thermochemical processes. A detailed MBM characterisation is essential to the understanding of MBM thermal processes and can help to avoid the difficulties involved in these processes.

The raw material is usually received as a powder with a particulate size varying between 5 and 3228 μm [8,11,17,21,29]. In some studies, the powder is pelletized [4,18] and the size of the pellet varies between 5 and 20 mm with a diameter of between 5 and 10 mm.

Table 1 displays the intervals for the proximate and ultimate analysis, and the heating values of the MBM used in several works. Furthermore, the fat and gross protein contents reported by Piazza and Garcia [30] are also included. The proximate and ultimate analysis (Table 1) shows high ash content, attributed to the presence of bones in the feedstock [4], and a high oxygen and nitrogen content. The broad interval found for several element and component contents, for example N, S and volatile contents, indicates the important variability in the MBM composition which will seriously

**Table 1**
Proximate and ultimate analysis, fat and gross protein content, and heating values of MBM [2,4,5,8,10,11,20,21,24,25,29,30,32–34].

| | Units | MBM |
|---|---|---|
| C | wt.% | 33.3–55.67 |
| H[a] | wt.% | 4.8–8.03 |
| N | wt.% | 0.43–10.4 |
| S | wt.% | 0.05–10.9 |
| O[b] | wt.% | 11.9–38.40 |
| Cl[c] | wt.% | 0.26–1.10 |
| Moisture | wt.% | 1.35–8.3 |
| Ash | wt.% | 10.38–34.4 |
| Volatiles | wt.% | 32.7–80.1 |
| Fixed carbon | wt.% | 2.8–26.1 |
| Fat | wt.% | 7.7–14 |
| Gross protein | wt.% | 48.7 |
| HHV | MJ/kg | 14.19–37.71 |
| LHV | MJ/kg | 13.06–30.29 |

[a] The wt.% of hydrogen includes the hydrogen of the moisture.
[b] Calculated by difference.
[c] Measured by X-ray fluorescence.

**Table 2**
Metal and trace element content (mg/kg) in MBM [4,7,16,35].

| Ca | P | Na | K | Mg | Fe | Zn | Mn | Cu | Cr |
|---|---|---|---|---|---|---|---|---|---|
| 67,207 | 31,842 | 8716 | 6339 | 1599 | 560.5 | 87.1–940 | 35.2 | <dl–270 | <dl–136.2 |
| Ti | Ni | Co | Pb | As | Se | Mo | Al | V | Cd |
| 3.5–725.4 | <dl–93.0 | 0.4–9.5 | <dl–<19.3 | <dl | <dl | <dl | <dl | 206.1 | <dl–0.3 |
| Ba | Bi | Ce | Cs | Ga | La | Sr | Sc | Rb | Y |
| 208.4 | 0.5 | 10.0 | 1.5 | 3.5 | 17.8 | 273.8 | 25.6 | 13.7 | 4.7 |

dl = detection limit.

influence MBM thermochemical treatments. The high amount of fat is also noticeable, and could be the reason for the poor bulk behaviour of the MBM, especially when the work temperature is above the melting point of the fat [31]. Due to the high protein content in the MBM (48 wt.%), Piazza and Garcia [30] studied the protein and gelatine extract as renewable flocculants.

Table 2 shows the interval for the metal and other trace element contents found in the literature. The evaluation of these data indicates the amounts of heavy metals in MBM are relatively low when compared with other materials such as coal, being Zn the exception [16].

Regarding MBM ash composition, more than 50 wt.% of the total ash quantities are calcium and phosphorus (Table 3). This is because the mineral content of bones is composed of calcium and phosphates. By means of the XRD method, Seneca [19] found that the only crystalline substance present in MBM is Apatite ($Ca_{10}(PO_4)_6(OH)_2$). Due to the chemical composition of MBM, Coutand et al. [7] and Deydier et al. [36] proposed the use of these ashes as a phosphate source for industry, agricultural soil enrichment or heavy metal immobilization in soil or water. Mondini et al. [26] and Jeng et al. [37,38] studied MBM soil application as a fertilizer, and concluded it is a promising strategy for a sustainable recycling of MBM given the high amount of nutritive content.

In thermal processes, calcium present in MBM can work as a catalyst [25] and can increase the gasification rate in gasification processes [17]. However, K, Cl and P in combination with Si and S are known to cause sintering and agglomeration problems inside reactors, while Ca could shift melting temperatures to a higher level [14,16].

Eljarrat et al. [39] evaluated the concentration of PCDDs (polychlorinated dibenzodioxins) and PCDFs (polychlorinated dibenzofurans) in several MBM samples. Previously to the analysis, fat extraction and purification of the extract was carried out. After that, purified PCDD/PCDF extracts were analysed by gas chromatography. The quantitative determination was performed by the isotope dilution method based on the relative response factor (RRFs). The results obtained are shown in Table 4. The major contribution in the total toxicity of the samples was found to be the 2,3,4,7,8-PeCDF congener. Eljarrat et al. [39] carried out a comparison among the results obtained from MBM and other samples such as animal fat, fish oil, and fish meal. The 2,3,4,7,8-PeCDF concentration (pg/g fat) found in the other samples were: 0.23–0.37 in animal fat samples, 1.10–1.93 in fish oil samples, and 0.8–6.9 in fish meal samples. These concentrations are similar and even higher than the 2,3,4,7,8-PeCDF concentration found in MBM samples (0.9–1.09 pg/g fat).

Besides chemical characterisation, physical characterisation of MBM is also necessary before its thermal treatments. In order to evaluate the flowability of the MBM, García et al. [31] evaluated the Hauser ratio of this raw material. The results obtained from this study show the fat content as the most significant factor in thermal behaviour of MBM. In this study, when the MBM fat content was reduced from 9.05 to 1.31 wt.%, the MBM classification in the Geldart range changed from difficult-to-fluidise (Group AC in Geldartĭs scheme) to easy-to-fluidise. Temperature has a progressive influence on the physical state of the fat, and thus on the behaviour of MBM. MBM fat is completely liquid at 55 °C, and the flowability of MBM at this temperature is worse than at lower temperatures [31]. The fat content can offer information about the MBM flowability inside the reactor.

## 3. Meat and bone meal thermochemical treatments

Energy potential uses of MBM by means of pyrolysis, combustion and gasification processes are currently being studied as an environmentally friendly alternative to land-filling. The products from these thermochemical processes are analysed as possible fertilizers (ash and liquid products) and fuels (gas and liquid products).

**Table 3**
Ash composition of MBM [10,13,14,17,33].

| | Units | MBM |
|---|---|---|
| Si as $SiO_2$ | wt.% | 0.80–5.97 |
| Ca as CaO | wt.% | 36.5–58.11 |
| Fe as $Fe_2O_3$ | wt.% | 0.11–0.7 |
| Al as $Al_2O_3$ | wt.% | 0.49–1.81 |
| Na as $Na_2O$ | wt.% | 0.78–9.0 |
| K as $K_2O$ | wt.% | 0.97–2.77 |
| P as $P_2O_5$ | wt.% | 35.65–37.30 |
| Mg as MgO | wt.% | 1.24–2.22 |
| Ti as $TiO_2$ | wt.% | 0.11 |

**Table 4**
PCDD and PCDF concentrations (pg/g fat) in samples of MBM [39].

| | MBM |
|---|---|
| 2378-TCDD | 0.2–0.38 |
| 12,378-PeCDD | 0.7–1.01 |
| 123,478-HxCDD | 1.1–2.52 |
| 123,678-HxCDD | 4.3–7.69 |
| 123,789-HxCDD | 1.2–1.37 |
| 1,234,678-HpCDD | 33.6–214.62 |
| OCDD | 264.0–2398.69 |
| 2378-TCDF | 1.4–3.05 |
| 12,378-PeCDF | 0.3–0.51 |
| 23,478-PeCDF | 0.9–1.09 |
| 123,478-HxCDF | 1.0–2.62 |
| 123,678-HxCDF | 0.6–1.41 |
| 234,678-HxCDF | 0.6–1.82 |
| 123,789-HxCDF | <0.1 |
| 1234678-HpCDF | 5.8–30.08 |
| 1,234,789-HpCDF | 0.5–2.70 |
| OCDF | 7.3–75.97 |
| I-TEQ | 2.72–8.50 |
| WHO-TEQ | 2.82–6.77 |
| R | 2.13–2.68 |

**Table 5**
Kinetic models analysed for combustion processes.

| | | Where: |
|---|---|---|
| Conesa et al. [5] | $-\frac{dw_i}{dt} = k_{io} \exp\left(-\frac{E_i}{RT}\right)(w_i - w_{i\infty})^{n_i}$ | $w_i$ is the weight fraction<br>$w_{i\infty}$ is the weight fraction at time infinity<br>$k_{io}$ is the pre-exponential factor<br>$E_i$ is the activation energy<br>$n_i$ is the reaction order<br>$R$ is the gas constant<br>$T$ the temperature |
| Senneca [19] | $\frac{df}{dt} = k'_o \exp\left(-\frac{E}{RT}\right) p_g^n$ | $k'_o$ is the pre-exponential factor<br>$p_g$ is the partial pressure of the reacting gas<br>$E_i$ is the activation energy<br>$n$ is the reaction order<br>$R$ is the gas constant<br>$T$ the temperature |

### 3.1. Combustion and co-combustion of meat and bone meal

Combustion and co-combustion of MBM with other materials, especially with coal, have been the most extensively studied treatments [5,6,10–14,16–20,24,29,33,34,36,40–44]. Most of these works have been performed in thermogravimetric systems and in fluidised bed reactors.

#### 3.1.1. Thermogravimentric studies

Preliminary studies about the thermal decomposition of MBM are necessary prerequisites for the understanding of MBM behaviour in these thermal processes. Some authors have analysed the thermal decomposition of MBM under combustion conditions [5,11,17,19,24,36,40]. Conesa et al. [5,11] developed experimental thermogravimetry (TG) and derivative thermogravimetry (DTG) curves for MBM combustion at 10, 20 and 30 K/min. The experiments were carried out in a thermobalance with synthetic air as atmosphere, using a flow rate of 20 ml/min and over a range of temperatures between 80 and 800 °C. A kinetic model and optimized values of the formal kinetic parameters were also obtained.

Senneca [19] carried out isothermal experiments of char combustion using TG/DSC equipment under reaction temperatures between 400 and 600 °C and with mixtures of oxygen in nitrogen (oxygen partial pressure of 0.1–0.21 bar). The analyses of the TG curves show a potential uptake of $O_2$ molecules and the formation of oxygenated compounds under oxidizing atmospheres. The comparison of the rate of MBM char combustion with different fuels indicates that at low temperatures MBM has a higher combustion rate (even two orders of magnitude higher than coal). However, the activation energy for MBM is low, and at high temperatures the rates of MBM char combustion become lower than coal char combustion rates. The peculiar behaviour of MBM is attributed to its high content in organics [19]. It is believed that the high mineral matter content of MBM enhances char combustion reactivity at low temperatures, but when the mineral matter transforms at higher temperatures char combustion reactivity is reduced.

Several authors have explained MBM behaviour by using a model comprising three different processes taking place when the material decomposes [5,19,40]. MBM thermal decomposition behaviour under combustion conditions suggests a first process between 30 and 200 °C where the animal flour dehydration takes place. In the second process, between 200 and 450 °C, light organic volatiles are released and the generated gases are burnt. The third process is a consequence of the degradation of the bone fraction and the complete decomposition of the remaining intermediates [4,17,40]. Furthermore, the thermally induced changes occurring in the organic and mineral phases of bone have been analysed by Essien Etok et al. [40]. The kinetic models studied and the optimized parameters for these models are shown in Tables 5 and 6 respectively. In both studies, authors described the MBM combustion process by means of a kinetic model consisting of a single reaction of $n$th order, similar one from other (see Table 5). However, Conesa et al. [5] consider the thermal decomposition of three fractions and specify the optimized parameter for each weight loss process (see Table 6), while Senneca [19] only consider one fraction. It can be observed that the main activation energy is required in the process between 200 and 450 °C corresponding to the burnt gases process.

In order to compare the emissions produced in the combustion of several wastes, Conesa et al. [24] analysed the PCDD/F composition of the flue gas obtained for different wastes in a thermobalance. The results show that the PCDD/Fs level (I-TEQ) found in MBM combustion are similar to the emission in the combustion of other raw materials such as sludge or lube oil.

#### 3.1.2. Meat and bone meal co-combustion in fluidised bed reactors

Co-combustion of MBM has been studied extensively in order to analyse the effect of adding MBM to coal combustion processes [10,13,14,16,18–20,29,34]. Some authors have studied the combustion of pure MBM and found that large agglomerates block the screw feeder and there are stickiness problems due to the MBM fat content [14,20,29]. Thus, co-combustion with coal and peat has been analysed. In the majority of these studies, the co-combustion of MBM with coal has been carried out in fluidised bed reactors with a continuous feed by means of a screw feeder [13,14,16,20,34], but pneumatic injection has also been used as an alternative feeding system [18].

Fryda et al. [13,14] studied the co-combustion of MBM with coal in a fluidised silica sand bed reactor. Different MBM with olive bagasse (OB) and two types of coal blends were analysed (10 wt.% of MBM–90 wt.% of coal, 20 wt.% of MBM–80 wt.% of coal, 20 wt.% of MBM–80 wt.% of OB and 40 wt.% of MBM–60 wt.% of OB) at different temperatures (between 850 and 890 °C) and equivalence

**Table 6**
Optimized parameters for kinetic models in combustion processes.

| | Conesa et al. [5] | Senneca [19] |
|---|---|---|
| $k_{01}$ (min$^{-1}$) | 7.16E3 | |
| $E_1$ (kJ/mol) | 30.9 | |
| $k_{02}$ (min$^{-1}$) | 4.84E5 | |
| $E_2$ (kJ/mol) | 72.2 | |
| $w_{20} - w_{2\infty}$ | 0.28 | |
| $k_{03}$ (min$^{-1}$) | 3.00 | |
| $E_3$ (kJ/mol) | 21.3 | |
| $w_{30} - w_{3\infty}$ | 0.32 | |
| $k' \times p^n$ (min$^{-1}$) | | 1.1E5 |
| $E$ (kJ/mol) | | 62.6 |
| $n$ | 1 | 1 |

ratios (between 1.3 and 1.78). Under these operational conditions, gaseous emissions (CO, $SO_2$, $NO_x$ and $N_2O$) and agglomeration tendencies were studied. The combustion efficiency achieved in the co-combustion experiments carried out in this study were between 0.99 in the test of 20 wt.% MBM–80 wt.% coal co-combustion and 0.86 in the 20 wt.% MBM–80 wt.% OB co-combustion test.

Senneca [19] analysed bottom and fly ashes and char composition in the 6 wt.% of MBM–94 wt.% of coal co-combustion test.

Gulyurtlu et al. [16] studied MBM/coal co-combustion at a temperature of 700 °C with silica sand as bed material. Gas emissions and the composition of the ashes collected in the cyclones, in the bed and from the stack were studied. In order to evaluate the suitability of depositing these ashes in municipal landfills, biological activity, ecotoxicity, heavy metals concentration and leachability were analysed.

Miller et al. [20] studied the effect on CO emissions of injecting feed material at different bed heights in a circulating fluidised bed combustor with sand as initial bed material. The fluidisation air velocity was 1.8 m/s and the bed temperatures were between 870 and 927 °C. The raw material was introduced into the reactor in a frozen state. Flue gas recirculation was applied in some of the tests and emission data collected and continuously analysed during each test.

McDonnell et al. [18,34] analysed gaseous emissions (CO, $SO_2$, $NO_x$, $N_2O$ and VOCs) and bed agglomeration tendencies for different feed compositions (from 15 wt.% of MBM to 35 wt.% of MBM with coal and 100 wt.% of MBM) [34]. The injection of the raw material in pellets in order to study the residence time was also carried out by these authors [18].

The main aim of these studies was to analyse how primary fuel substitution by MBM can affect flue gas emissions, ash composition, and fluidised bed agglomeration tendency, in order to evaluate MBM co-combustion as an alternative to land-filling.

*3.1.2.1. Emissions.*

*3.1.2.1.1. CO emissions.* The results obtained by several authors show that CO emissions increase with higher fluidisation velocities due to the reduced residence time [13,14] and increase with MBM percentage [13,14,16,34]. This is attributed to the higher MBM volatiles content which provokes high hydrocarbon concentrations in the combustion atmosphere. This fact suppresses the further oxidation of CO that normally occurs through reactions (1) and (2) with oxygenated free radicals HO and $HO_2$ [14].

$$CO + OH \leftrightarrow CO_2 + H \quad (1)$$

$$CO + HO_2 \leftrightarrow CO_2 + HO \quad (2)$$

The feed location and the operational temperature also affect CO emissions [20]. When fuel is fed directly into the bed, CO emissions are lower than the emissions produced when the raw material is fed overbed (22% increment). CO emissions increase when the operational temperature decreases.

The influence of the flue gas recirculation (FGR) on CO emissions was studied by Miller et al. [20] by means of a statistical method (ANOVA). The data showed that FGR significantly affects to the CO level. CO emissions were reduced by 59.3 vol.% when the fuels were fired with FGR.

Fig. 3 shows the CO concentration in ppm (parts per million) found in the various studies.

*3.1.2.1.2. $SO_2$ emissions.* Some authors confirm that emissions of $SO_2$ may be reduced when MBM is added to coal processes because of the sulphur content in the fuel decreases with the addition of MBM [13,14,16,20,34]. Furthermore, $SO_2$ also depends on ash derived CaO that acts as a natural desulphuriser. Despite that, no significant effect on desulphurisation was found by the MBM addition [14,16]. Fryda et al. [14] indicated two effects of MBM

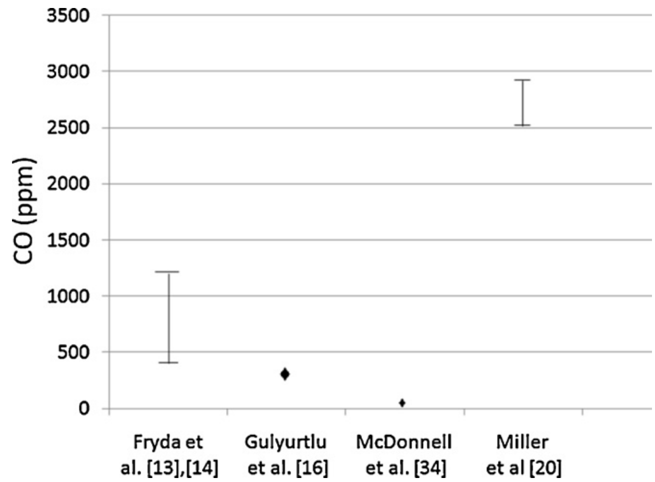



**Fig. 3.** CO concentration in several operational conditions: 6% $O_2$ and 20 wt.% of MBM with coal (Fryda et al. [13,14]), 11% $O_2$ and 20 wt.% of MBM with coal (Gulyurtlu et al. [16]), 6% $O_2$ and 20 wt.% of MBM with peat (McDonnell et al. [34]), 3% $O_2$ and 17–22 wt.% of MBM with coal (Miller et al. [20]).

ashes that possibly hinder desulphurisation. Firstly, the large particles of MBM used tend to accumulate in the bottom of the bed and remain practically inactive. Secondly, Ca formed Ca-phosphate in MBM. This is a very stable phase under combustion conditions and therefore not chemically active as a desulphurisation agent. On the other hand, Fryda et al. [14] also observed that the desulphurisation effect can also be hindered by the increase in volatiles with the MBM addition. McDonnell et al. [34] explained that the presence of HCl promotes $SO_2$ capture by bed material and fly ash particles, since the Cl content is higher in MBM than in coal. The MBM addition thus results in a reduction of $SO_2$ emissions.

Fig. 4 shows the $SO_2$ concentrations found in the various studies.

*3.1.2.1.3. $NO_x$–$N_2O$ emissions.* The nitrogen content in MBM is higher than in coal. For this reason, the introduction of small percentages of MBM into coal fuel can cause an increase in $NO_x$ and $N_2O$ emissions [13,14,16]. Besides, the small quantities of MBM introduced into non-volatile fossil do not increase enough volatiles to activate the $NO_x$ destruction mechanism [14]. However, Gulyurtlu et al. [16] described an important reduction in $NO_x$ emissions for MBM–coal blends with a percentage of MBM higher than 20 wt.% when the temperature was above 1000 °C. A significant part of the nitrogen content in the fuel was able to be released as $NH_3$, and

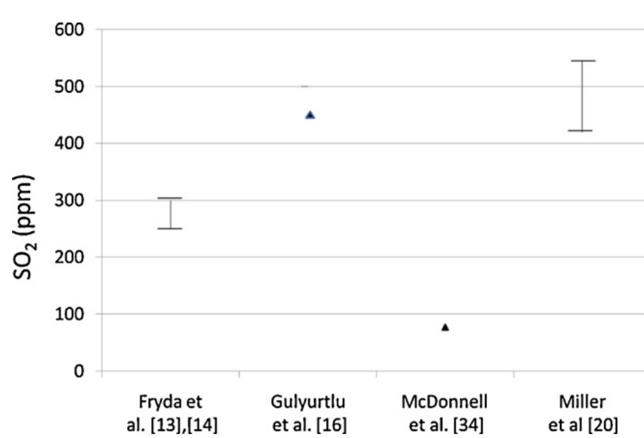



**Fig. 4.** $SO_2$ concentration in several operational conditions: 6% $O_2$ and 20 wt.% of MBM with coal (Fryda et al. [13,14]), 11% $O_2$ and 20 wt.% of MBM with coal (Gulyurtlu et al. [16]), 6% $O_2$ and 20 wt.% of MBM with peat (McDonnell et al. [34]), 3% $O_2$ and 17–22 wt.% of MBM with coal (Miller et al. [20]).

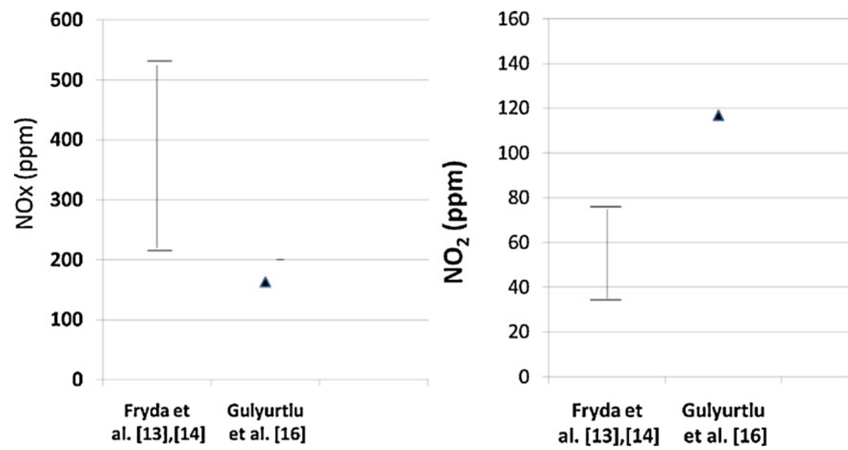



**Fig. 5.** $NO_x$ (figure a) and $NO_2$ (figure b) concentration in several operational conditions: 6% $O_2$ and 20 wt.% of MBM with coal (Fryda et al. [13,14]) and 11% $O_2$ and 20 wt.% of MBM with coal (Gulyurtlu et al. [16]).

reacted with $NO_x$ by reducing it to $N_2$ through the $NO_x$ mechanism [16].

$N_2O$ and $NO_x$ emissions can be reduced due to the catalytic effect of char and CaO rich ashes. This effect is significant when the bed operates with a higher char inventory [13,14]. As is well known, $N_2O$ emissions are also sensitive to temperature; a temperature increase causes $N_2O$ emissions to drop. Fig. 5 shows the $NO_x$ and $NO_2$ concentrations found in the various studies.

*3.1.2.1.4. VOCs emissions.* Concentrations of volatile organic compounds (VOCs) in the flue gas was higher when 100 wt.% of MBM rather than a MBM–coal blend was combusted [34]. However, although the MBM increased the VOC emissions, the levels of these emissions were below the limit of 20 mg/m$^3$ permitted in the European Union [34].

*3.1.2.1.5. PCB, PCDD and PCDF emissions.* Dioxin and furans emissions have been studied by several authors [12,24,33,34,41]. Gulyurtlu et al. [41] reported that the substitution of coal with MBM may increase PCDD and PCDF production. This increase could be due to the chlorine content in the fluidised bed reactor being related with the PCDD and PCDF emissions [34].

Lopes et al. [33] reported that the PCDD/F level ranged from 6% when coal was combusted alone to 97.3% of the total PCDD/F accounted for when MBM was combusted alone.

In general, the emissions were predominantly below regulatory limits [34].

*3.1.2.2. Ash composition and uses.* MBM combustion ashes have been extensively studied in order to analyse their potential uses as fertilizer or hazardous immobilizing material for pollutants present in aqueous solutions. Ash analysis has shown a high content in phosphorus, found mainly in the cyclone ashes [34]. In general, increasing the proportion of MBM in co-combustion processes with coal increased the As, P and Ni concentrations in the leachate from the cyclones ashes [34].

Gulyurtlu et al. [16] analysed the chemical composition, leachability, ecotoxicity and protein concentration of the ashes from the bed and cyclones. The quantity of bed ash produced increased with the MBM percentage in the MBM–coal blends, while the particle diameter of the ashes collected in the cyclones decreased as the MBM percentage increased [16]. Elemental composition of the ashes was affected by the MBM presence in the blends. Carbon content in the ashes decreased while phosphorus and sulphur content increased as the MBM percentage increased in the blends burned [16]. Furthermore, Senneca [19] found that the carbon content in the bottom ashes (2 wt.%) was lower than the carbon found in the fly ashes (8–11 wt.%). The release of chloride (Cl) has been found to be higher when the percentage of MBM was increased in the mixture burned; however, even the ashes obtained from 100% MBM are within the permitted limits of non-hazardous residues [16].

Another potential use of MBM combustion ashes is as a hazardous immobilizing material in polluted aqueous solutions [42–44]. Deydier et al. [42,43] analysed the ability of MBM ashes to remove lead from aqueous effluents. The mechanistic study revealed that lead is immobilized as pyromorphite and lead carbonate dehydrate. Thus, MBM combustion ashes could be used as a low cost substitute for synthetic apatite. Furthermore, Coutand et al. [44] demonstrated the efficiency of MBM ash from combustion processes in removing cadmium from aqueous solutions.

Paisley and Hostrup-Pedersen [6] developed simulation models to estimate the degree of Bovine Spongiform Encephalopathy infectivity contained in the fly ashes from MBM combustion. The results suggested the risk from using fly ash for the phosphate or fertilizer industry is negligible because of the remote possibility of infectivity.

Hence, it may be concluded that most MBM ashes could be safely accepted in normal municipal landfills or, taking into account their high phosphorus content, could be used as solid fertilizer or as pollutant remover from aqueous solutions [7,42].

*3.1.2.3. Agglomeration tendencies.* Agglomeration problems have been described in the combustion and co-combustion of MBM and are attributed by several authors to the high fat content in MBM [13,14,16,20]. Gulyurtlu et al. [16] described important agglomeration inside the bed at temperatures above 820 °C. This agglomeration provoked defluidisation of the bed. Miller et al. [20] reported several difficulties in mixing MBM with sand due to the density of the bed, but these were solved by means of overbed feeding of the MBM. Fryda et al. [13,14] described the conglomerates as small particles of bone and sand fragments with a particle diameter between 1 and 50 μm when MBM was co-combusted with coal in a fluidised bed combustor. However, although defluidisation may take place when MBM is added to coal combustion processes, the Al and Ca content in the ash provides a remedy against severe agglomeration by preventing the formation of alkali silicates which melt at low temperatures [13,14]. Although severe bed agglomeration can be avoided when appropriate coal and MBM blends are co-combusted, agglomeration and total defluidisation caused by sintering of ash and bed particles has been observed in olive bagasse–MBM co-combustion [14]. At elevated temperatures, the Si present in the fuel can produce eutectics of Si and alkalis to form a liquid phase that is sticky and highly viscous [14].

**Table 7**
References summary of MBM co-combustion process studies in which the effect of some variables on important parameters is analysed.

| On\influence of | %MBM | *T* | ER | Fixed carbon in the bed | Feed location | Flue gas recirculation |
|---|---|---|---|---|---|---|
| Activation energy of the char | | [19] | | | | |
| Ash characterisation | [16,19,41] | [36] | | | | |
| Ash composition | [13,19] [16,34] | [36] | | | | |
| CO, $CO_2$ emissions | [13,14,16,20,29,34,41] | [20] | [13] [14] | | [20] | [20] |
| $SO_2$ emissions | [13,14,16,20,34,41] | | [13] [14] | | | |
| $NO_x$–$N_2O$ emissions | [13,14,16,20,34] | | [13] [14] | [13] [14] | | |
| PCB, PCDD, PCDF and PM emissions | [30,32,41] | [24] | [24] | | | |
| VOCs emissions | [16,34,41] | | | | | |
| Agglomeration bed characterisation | [13,14] | | | | | |
| Combustion efficiency | [14] | | | | | |
| Solid residence time | [18] | | | | | |

In addition to studying several variables such as emissions, ash characterisation and composition, some authors have analysed the effect of certain factors on these important variables. Table 7 provides a summary of the effects of several factors on different variables of the MBM co-combustion process.

### 3.2. *Pyrolysis and co-pyrolysis of meat and bone meal*

MBM pyrolysis has been studied, up to now, by means of thermogravimetric studies and in fixed bed reactors, in a laboratory scale, as explain below.

#### 3.2.1. *Thermogravimetric studies*

In order to characterise the behaviour of MBM in pyrolysis processes, some authors have studied the thermal decomposition of MBM by means of TG (thermogravimetric) and DTG (differential thermogravimetric) analysis in nitrogen atmospheres [4,5,8,11,17,19,35]. TG and DTG analyses have been carried out by Chaala and Roy [4], Ayllón et al. [8], Conesa et al. [11] and Skodras et al. [17,35]. Three different zones can be distinguished in the curves obtained in these analyses (see Fig. 6). The sample dehydration occurs up to 148 °C. The weight loss from 148 to 225 °C is attributed to the evaporation of low molecular weight compounds and decomposition reactions. The highest weight loss rate is estimated in the temperature range of 200–400 °C and is

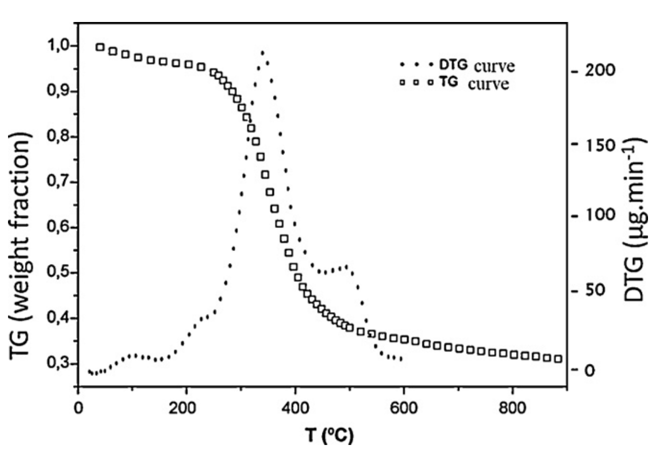



**Fig. 6.** Decomposition curve obtained by Ayllón et al. [8] in TG and DTG analysis with a heating rate of 10 °C/min.

due to degradation reactions in which the organic intermediates are destroyed. A shoulder is observed at 360–500 °C that probably corresponds to the degradation of the bones. The last part of the decomposition takes place from 600 to 900 °C.

Skodras et al. [17] compared DTG curves from MBM pyrolysis and DTG curves from several MBM/coal blends (10, 20, 30 and 50 wt.% of MBM). Significant interactions took place during the pyrolysis process of coal–MBM blends. An increase in the MBM present in the coal–MBM blends caused a rise in the weight loss rate (%/min) in the temperature range of 200–450 °C, reflecting the increase in the reactivity. Senneca [19] compared the DTG curves produced in the pyrolysis of MBM under inert (100% $N_2$ or He) and oxidative conditions (7%, 10% and 21% $O_2$ in He). When pyrolysis was carried out under oxidative conditions, one stage of weight loss was observed peaking at a moderately higher temperature than under inert conditions. A marked stage of weight loss at temperatures higher than 550 °C occured under oxidative atmospheres.

##### 3.2.1.1. *Kinetic models of MBM pyrolysis process.*

By means of these thermal decomposition studies, Conesa et al. [5], Ayllón et al. [8], Senneca [19] and Skodras et al. [35] have developed kinetic models for the pyrolysis reactions.

The pyrolysis tests were conducted at standard pressure, over the temperature range of around 100–800 °C [5,19] and 30–1000 °C [8,35], at different heating rates between 5 and 20 °C/min [8,19] and 5–100 °C/min [35] with a particulate size between 150 and 350 µm. The results obtained from the pyrolysis under inert conditions ($N_2$) showed a first order reaction model, which considers two, three [5,19] and four [8,35] fractions decomposing simultaneously. Ayllón et al. [8] tested several models but the results obtained shown that the four fractions model produce a better correlation with the experimental results. These conversion derivatives ($d\alpha/dT$) versus the temperature curves are shown in Fig. 7.

Tables 8 and 9 show the kinetic models and the optimized parameters for these kinetic models chosen by the different authors [5,8,19,35]. As can be observed, the kinetics parameters obtained by Ayllón et al. [8] are similar to the parameters found by Conesa et al. [5]. The slight differences could be due to the differences in the MBM composition used in each of these experimental works.

Senneca [19], comparing pyrolysis and combustion, observed that for the first stage of weight loss, the apparent activation energy decreased with the concentration of oxygen in the gaseous atmosphere (from 213.18 kJ/mol in $N_2$ conditions (Table 9),

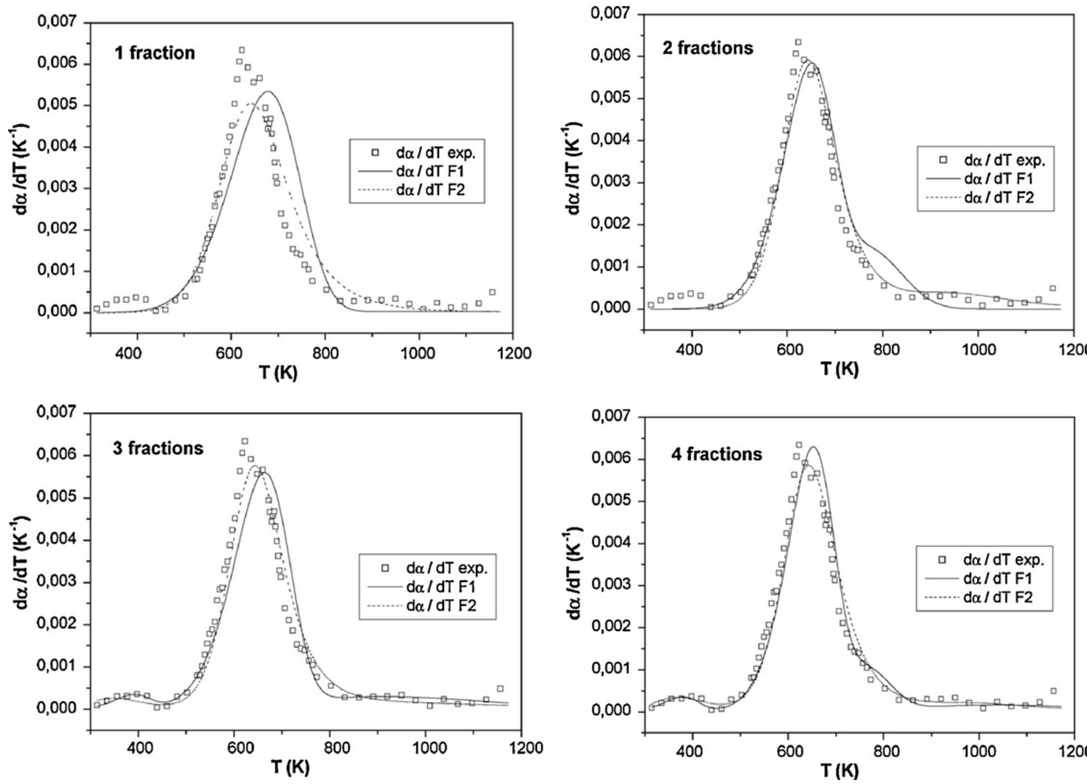



**Fig. 7.** Decomposition rate curve comparison between first order equation (F1) and second order equation (F2) at 15 °C/min heating rate (Ayllón et al. [8]).

to 129.58 kJ/mol in 21% $O_2$ conditions) and the reaction order decreased with the oxygen concentration. The reason could be that oxygen complexes may alter the dependence of the pyrolysis rate on the temperature.

*3.2.2. Meat and bone meal pyrolysis in fixed bed reactors*

The studies to date of the MBM pyrolysis process in order to analyse the products obtained have been developed in batch laboratory reactors [4,25]. Chaala and Roy [4] and Ayllón et al. [25] used a fixed

**Table 8**
Kinetic models proposed for pyrolysis processes.

| | | Where: |
|---|---|---|
| Conesa et al. [5] | $-\frac{dw_i}{dt} = k_{io}\exp\left(-\frac{E_i}{RT}\right)(w_i - w_{i\infty})^{n_i}$ | $w_i$ is the weight fraction<br>$w_{i\infty}$ is the weight fraction at time infinity<br>$k_{io}$ is the pre-exponential factor<br>$E_i$ is the activation energy<br>$n_i$ is the reaction order<br>$R$ is the gas constant<br>$T$ the temperature |
| Ayllón et al. [8] | $\frac{d\alpha}{dT} = \frac{1}{1-f_\infty}\sum_{i=1}^{N}\frac{d\alpha}{dT}(f_{io} - f_{i\infty})$<br>and<br>$\frac{d\alpha_i}{dT} = \frac{k_{io}}{\beta}e^{-E_{i_i}/RT}(1-\alpha_i)$<br>and<br>$\alpha = \frac{w_o - w_t}{w_o - w_\infty}$ | $f$ is the weight fraction<br>$w_o$ is the initial weight fraction<br>$w_t$ is the weight at any time<br>$w_\infty$ is the weight at the end of the experiment<br>$\beta$ is the heating rate<br>$k_{io}$ is the pre-exponential factor |
| Senneca [19] | $-\frac{1}{m_o}\frac{dm}{dt} = k_o\exp\left(-\frac{E}{RT}\right)\left(1-\frac{m_\infty}{m_o}\right)^n$ | $k_o$ is the pre-exponential factor<br>$m_o$ is the initial weight of sample<br>$m_\infty$ weight of sample residue<br>$E$ is the activation energy<br>$n$ is the reaction order<br>$R$ is the gas constant<br>$T$ the temperature |
| Skodras et al. [35] | $-\frac{dm}{dT} = \sum_i c_i\frac{da}{dT},\ i = 1, \ldots, N$<br>and<br>$\frac{da}{dT} = A_i\exp\left(-\frac{E_i}{RT}\right)(1-a_i)$<br>and<br>$c_i = m_{oi} - m_{char,i}$<br>$a_i = \frac{m_{oi}-m_i}{m_{oi}-m_{char,i}}$ | $m_o$ is the initial dry sample mass<br>$m_{char,i}$ is the final char yield of the $i$ component<br>$A_i$ is the pre-exponential factor<br>$E$ is the activation energy<br>$R$ is the gas constant<br>$T$ the temperature |

**Table 9**
Optimized parameters for kinetic models in pyrolysis processes.

| | Conesa et al. [5] 10 K/min | Ayllón et al. [8] 20 °C/min | Senneca [19] 5 °C/min | Skodras et al. [35] 20 °C/min |
|---|---|---|---|---|
| $f_{io} - f_{i\infty}$ | | 0.060 | | |
| $A_1$ (min$^{-1}$) | | | | 5.3E6 |
| $k_{01}$ (min$^{-1}$) | 7.13E3 | | 7.2E17 | |
| $E_1$ (kJ/mol) | 30.9 | | 213.18 | 66.9 |
| $c_1$ (%) | | | | 17.2 |
| $A_2$ (min$^{-1}$) | | | | 1.8E11 |
| $k_{02}$ (min$^{-1}$) | 4.84E5 | | 7.4E11 | |
| $E_2$ (kJ/mol) | 72.2 | | 154.66 | 132.9 |
| $c_2$ (%) | | | | 23.1 |
| $A_3$ (min$^{-1}$) | | | | 2.1E15 |
| $k_{03}$ (min$^{-1}$) | 3.00 | | | |
| $E_3$ (kJ/mol) | 21.3 | | | 199.5 |
| $c_3$ (%) | | | | 39.4 |
| $A_4$ (min$^{-1}$) | | | | 6.1E3 |
| $k_{04}$ (min$^{-1}$) | | 6.00 | | |
| $E_4$ (kJ/mol) | | 39.00 | | 57.6 |
| $c_4$ (%) | | | | 15.1 |
| $\alpha$ | | 0.999 | | |
| $d\alpha/dT$ | | 0.976 | | |

bed reactor for MBM, heated by an electrical tubular furnace, with different capacity. Chaala and Roy [4] studied vacuum pyrolysis at 500 °C and 15 °C/min of 516.5 g of pelletized MBM. Ayllón et al. [25] performed ambient pressure pyrolysis of 30 g of MBM powder (particle size lower than 3 mm) at different heating rates (2–14 °C/min) and temperatures (300–900 °C). The pyrolysis products obtained (solid, liquid or tar and gas) were collected separately for analysis in both works [4,25]. Tar was collected in cold gas traps connected in series with the reactor, and gas composition was analysed by GC–MS [4] or by GC-TCD [25].

Ayllón et al. [25] analysed the influence of the pyrolysis temperature and heating rate on the product yield, but also on gas, tar and char composition, gas heating value, cold gas efficiency and on the specific surface area of the char. This is the only work that studies the influences of important pyrolysis variables on several parameters of the pyrolysis process.

*3.2.2.1. Products from the pyrolysis process.* The product yields obtained in vacuum pyrolyisis by Chaala and Roy [4] at 500 °C were: 37.1 wt.% of pyrolytic oil, 39.1 wt.% of solid residue, 11.6 wt.% of aqueous phase and 9.4 wt.% of gases. Ayllón et al. [25] analysed the effect of the pyrolysis temperature (300–900 °C) on the product yields. The main products obtained at any temperature were liquid (tar) and char. The results obtained show the gas yield increased with the temperature up to approximately about 20 wt.% at 900 °C. The char yield decreased with temperature (from 48 wt.% at 300 °C, to 30 wt.% at 900 °C) while the tar yield increased until 450 °C (from 45 wt.% at 300 °C to 55 wt.% at 450 °C) after which its value remained practically constant. Since the effect of the heating rate on product distribution was also studied by Ayllón et al. [25], it can be observed that the temperature has a much greater effect than the heating rate in the intervals analysed in this work.

Fig. 8 shows the product distribution in the pyrolysis processes carried out by Chaala and Roy [4] and Ayllón et al. [25]. The data correspond to pyrolysis at 500 °C.

The main data reported for MBM pyrolysis products are summarised in the following paragraphs.

*3.2.2.1.1. Condensable product.* The liquid product was the main product obtained in the pyrolysis experiments performed. Ayllón et al. [25] observed that approximately 30 wt.% of the total liquid produced was depleted in the 250–300 °C range, and more than 50 wt.% of the tar was produced below 300 °C. The physicochemical properties of the pyrolytic oil have also been analysed [4]. Pyrolytic liquid is dark, has an unpleasant smell and is highly viscous (609 cS at 50 °C). This oil has 3.4 wt.% of water content and its pH is 6.9. Although the nitrogen content is high (14 wt.%), the high heating value (34.2 MJ/kg) and the low carbon residue (4.5 wt.%) suggest that this oil could be used as an alternative fuel in boilers or gas turbines [4,25].

The pyrolysis liquid composition has been analysed by means of GC–MS [4,25] and GC-FID [25]. Nitrogenated aliphatic compounds were the most abundant at any temperature range (reaching about 83% of the tar production at 500–550 °C) [25]. Ayllón et al. [25] also studied the effect, at several temperatures, of the heating rate on the tar composition. No effect was observed.

*3.2.2.1.2. Solid product.* The solid residue has been described as a hard and easily breakable carbonaceous mass [25]. Some metals are contained in the ashes of this solid pyrolysis residue and could be used as catalyst in gasification processes. Thus, the char composition has been studied in order to analyse the evolution of the amount of ash obtained. The ash percentage increased from 47.26 wt.% at 300 °C to 55.88 wt.% at 825 °C [25]. The effect of the heating rate on the char composition resulted in a higher ash content at high heating values.

The effect of the heating rate value on the char morphology has been observed by means of SEM images (scanning electron microscopy) [25]. Ayllón et al. [25] also performed BET analysis on the MBM char. The results show that at middle-high temperatures (450–600 °C), the specific surface area increased when the heating rate decreased. The specific surface area increased from 600 to 900 °C, reaching its maximum value of 37.7 $m^2$/g at 900 °C.

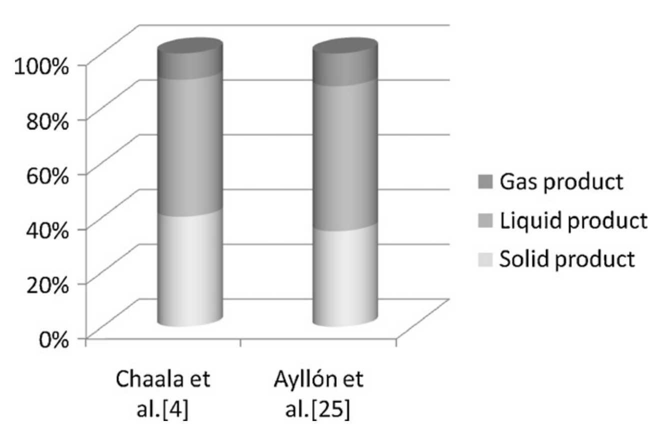



**Fig. 8.** Product distribution obtained in pyrolysis processes in fixed bed reactors, reported by Chaala and Roy [4] at 500 °C and 4 kPa, and Ayllón et al. [25] at 500 °C and 101.325 kPa.

Although the low specific surface area indicates that this solid is not suitable for use as an absorbent, the mineral composition of the solid residue has been analysed in order to identify other possible uses. Due to the high NPK content (nitrogen 4–7 wt.% dry basis, phosphorus 26 mg/kg and potassium, 529 mg/kg) [4], this solid residue could be an effective fertilizer. Furthermore, its high compressive strength and low water absorption capacity suggest it is a possible aggregate for concrete manufacturing [4].

*3.2.2.1.3. Gas product.* The results obtained by Ayllón et al. [25] show the lower heating value of the gas increased up to 600 °C (16 MJ/m$^3$ NTP). The cold gas efficiency increased with the temperature, and the maximum value obtained was about 12% at 900 °C.

The compounds analysed in the gas product (in a nitrogen free basis) were [25]: $CO_2$, CO, $CH_4$, $H_2$, $C_2H_4$, $C_2H_6$, $C_2H_2$ and $H_2S$. At low temperatures, $CO_2$ was the most abundant gas, but it decreased when the temperature increased (from 80 to 30 vol.%). This could be due to the evaporation of low molecular weight compounds at low temperatures, as well as decomposition reactions with the scission of C–C bonds [8]. Although smaller amounts of $CO_2$ were produced when the temperature increased, the amount of CO increased. Chaala and Roy [4] carried out a nitrogen balance indicating that 91.6 wt.% of the nitrogen present in the raw material was recovered in the liquid product and the solid residue, while a low amount of this nitrogen (6.6 wt.%) was recovered in the gas product. Due to its low nitrogen content and the heating value, this gas could be co-fired to provide heat for the pyrolysis process.

Apart from the pyrolysis gas product study developed by Ayllón et al. [25], emissions produced from MBM pyrolysis have been evaluated by Conesa et al. [11,24]. The pyrolyis experiments were carried out in a horizontal furnace at temperatures between 450 and 1100 °C [11,24]. A sample of 0.1–0.2 g of MBM was introduced into the furnace and kept there from 5 to 20 min. The gas produced in each test was collected in an adsorbent trap and extracted using toluene. High resolution gas chromatography and high resolution mass spectrometry for dioxin and furans analysis were performed. The results show that the maximum I-TEQ value found in the pyrolysis of MBM (20.2 pg/g at 850 °C) [11] was higher than the I-TEQ value found in the raw material (2.72–8.50 pg/g) [39]. However, a comparison among PCDD/Fs produced in the pyrolysis of MBM and other pyrolysis wastes show that the total PCDD/Fs produced in MBM pyrolysis were 10 and 20 times lesser than the amount produced in sewage sludge and PVC pyrolysis, respectively.

### 3.3. Gasification and co-gasification of meat and bone meal

Up to now, the gasification and co-gasification of meat and bone meal has been developed by means of thermogravimetric studies and in fluidised bed reactors. In the present section, a detailed summary of these studies is introduced.

#### 3.3.1. Thermogravimetric studies

Senneca [19] studied the instantaneous rate of gasification of char from MBM with $CO_2$. The results show that the reaction rate initially decreased with the char conversion. Notably low values of activation energy were obtained (75.14 kJ/mol) in this gasification research.

#### 3.3.2. Studies in bench scale plants

There are few works about MBM gasification and co-gasification [2,15,21], and most have been performed in bench scale plants [2,21]. These gasification studies in laboratory installations have been carried out using different types of reactors, including fixed bed [21] and fluidised bed reactors [2]. The objective of these works was to analyse MBM gasification products.

Soni et al. [21] analysed the gasification process of MBM in a fixed bed reactor and evaluated the effect on the process of adding a second fixed bed reactor for thermal cracking of tar produced in the first stage. The reactors were heated by electrical furnaces with a heating rate of 25 °C/min, and 2 g of MBM dust samples were placed on a plug inside the first reactor in a non-continuous way. The experiments were carried out at temperatures between 650 and 850 °C during 30 min. The vapours produced were conducted to glass condensers where the tar was picked up. The gas collected was measured and analysed using gas chromatograph units. Soni et al. [21] evaluated the product yields and the gas heating value obtained with these two fixed bed reactors in series and compared the results with those obtained in a single stage reactor. Furthermore, the effects of the equivalence ratio (ER) and of the packed bed height of the second reactor were also studied.

The gasification of MBM in a fluidised bed reactor with nitrogen and steam as gas carriers was evaluated by Fedorowicz et al. [2]. Both gases entered the reactor from the bottom with a total flow rate of 2.48 l/min of nitrogen and 0.1 ml/min of steam. The reactor was heated up to 1000 °C using an electrical furnace. When the reactor reached this temperature, the MBM was fed to the sand bed, in a non-continuous way, by means of a brass plunger and a ball valve system. The sample of MBM was a 9 g frozen sample. The gas flow produced in the gasification reactions was cleaned of solid particulates and analysed in a gas chromatograph unit. The solid residue (char) remaining in the reactor after dismantling was collected and analysed in a CHN analyser.

*3.3.2.1. Products in the gasification process.* Soni et al. [21] analysed the effect of the temperature, the equivalence ratio, the addition of a secondary fixed bed reactor stage, and the secondary bed height on the product yields. The gas yield varied from 22.1 wt.% at 650 °C to 30.8 wt.% at 850 °C while the tar and char decreased from 47 and 22.9 wt.% at 650 °C to 40.7 and 17.8 wt.% at 850 °C, respectively [21]. Besides, it was observed that the gas yield increased from 43.3 to 56.2 wt.% when the ER increased from 0.15 to 0.3, while the char and tar yields decreased. The two-stage process proved to be effective to increase the gas yield and to decrease the tar yield, 16.8 and 21.4 wt.% respectively. Finally, Soni et al. [21] observed that the gas yield barely increased with the secondary bed height while the tar yield decreased when this bed height was varied from 40 to 100 mm.

The main data reported about MBM gasification products are summarised in the following paragraphs.

*3.3.2.1.1. Gas product.* Gas composition was studied by Soni et al. [21] and Fedorowicz et al. [2]. Product gas was mainly composed of $H_2$, CO, $CO_2$, $CH_4$ and other heavier hydrocarbon gases.

The results of the experiments performed in the fixed bed reactors [21] show $CO_2$ yield decreased with temperature, from 55 to 20.5 vol.% ($N_2$ free basis) whereas CO yield increased from 10 to 51.6 vol.% [21]. This tendency is due to the Boudouard reaction ($C + CO_2 \leftrightarrow 2CO$) that connects CO and $CO_2$ yields. However, both CO and $CO_2$ increased when the equivalence ratio increases [21].

Fedorowicz et al. [2] carried out tests to compare the gas produced from MBM and the gasification of other animal wastes. The results show that MBM produces a smaller amount of gas (5.5 ft$^3$/lb fuel) than other wastes (7.5 ft$^3$/lb fuel) and relate the hydrogen content in the product gas with the hydrogen content in the raw material. The linearity between the increase in hydrogen in the product gas with the increase in hydrogen in the fuel shows that the hydrogen yield is a function of the fuel content. The gas heating value found in the MBM gasification was 430 Btu/ft$^3$ ($N_2$ free basis).

*3.3.2.1.2. Solid product.* Char produced in MBM gasification processes has hardly been studied. Fedorowicz et al. [2] collected a sample of this type of char and its ultimate analysis revealed a C content of 18.7 wt.% and low nitrogen and hydrogen contents (1.6 and 0.9 wt.%, respectively).

**Table 10**
$NO_x$ and $SO_x$ emissions [15].

| Emission | Regular test | MBM test | 88/609/EEC |
|---|---|---|---|
| $NO_x$ (mg/N m$^3$) | 100 | 74 | 650 |
| $SO_x$ (mg/N m$^3$) | 50 | 60 | 400 |

*3.3.2.1.3. Liquid product.* Liquid fraction produced in MBM gasification has not been studied.

Fedorowicz et al. [2] explained that the tar produced in the gasification process was produced from the fat contained within the fuels. The fat quickly pyrolyses in the gasifier producing volatiles containing hydrocarbons of high molecular weight that condense throughout the system when the gas temperature decreases. Thus, tar fraction is very difficult to be collected and no tar analyses have been published in the literature to date.

### 3.3.3. Studies in a commercial plant

MBM with a blend of coal and petroleum coke (fuel) was co-gasified in an IGCC (Integrated Gasification Combined Cycle) plant [15] in order to evaluate the viability of this co-gasification to achieve a combustible gas free of pollutants, which can be burned with high efficiency in a combined cycle electricity-generating unit. The MBM–fuel was pressurized and continuously fed into the reactor of 28.5 kg/s by means of a pneumatic pump (gasifier pressure = 25 bar). Syngan was produced by the reaction of these blends (1% MBM–99% fuel and 4.5% MBM–95.5% fuel) with oxygen and steam at temperatures up to 1600 °C. Gas, liquid products (tar and water) and ash were analysed.

García-Peña and Muñoz Mozos [15] studied the emissions produced when the MBM–fuel blend gas was combusted in the IGCC plant gas turbine. The $SO_x$ and $NO_x$ emissions measured in MBM tests and in regular fuel operation tests can be seen in Table 10, together with the maximum levels of both pollutants permitted by European regulations. The $NO_x$ emission value for MBM was lower than that produced in the regular fuel gasification. The $SO_x$ value was higher but within permitted limits.

García-Peña and Muñoz Mozos [15] also collected slag and fly ash samples produced in the IGCC process. Table 11 displays the Na, Ca and P contents (expressed as oxides) in slag and fly ashes for the gasification test performed with regular fuel and with blends of MBM. These data show Na compounds in MBM tests are higher than in regular fuel tests. This could be due to the raw material composition. Phosphorous contained in the MBM raw material transferred to the fly ash rather than the liquid product.

Water fraction produced in MBM co-gasification was also analysed by García-Peña and Muñoz Mozos [15] and its composition compared with the tar composition obtained in the regular fuel gasification process. A higher value was found in the $Cl^-$ analysis, due to the raw material composition.

In conclusion, tests carried out in the IGCC plant demonstrated the technical viability of MBM co-gasification with regular fuel used in this plant (coal, pet coke and limestone). A negligible efficiency variation (from 0.75 to 0.74) was found when MBM (1 and 4.5 wt.%) was added to the process.

In addition to the study of variables such as product distribution or gas composition, some authors have analysed the effect of various factors on these important variables. Table 12 shows a summary of the variables studied in the gasification processes together the influence of some factors on the different variables.

## 4. Needs

Although MBM combustion has been extensively studied, there are very few MBM pyrolysis and gasification studies. All the studies published about combustion, pyrolysis and gasification of MBM have been carried out in fixed and/or in fluidised bed reactors. However, other types of biomass, as forest biomass, sewage sludge or straw black liquor and coal, are also being managed in circulating fluidised bed, spouted bed and rotating reactors [45–49]. Moreover, pyrolysis and gasification processes with continuous feeding

**Table 11**
Fly ash and slag composition [15].

| Residue | Operation | CaO (wt.%) | $Na_2O$ (wt.%) | $P_2O_5$ (wt.%) |
|---|---|---|---|---|
| Fly ash | Regular fuel | 2.5–4.0 | 0.4–0.5 | 0.4–0.6 |
| | 4.5% MBM test | 3.3 | 0.7 | 1.1 |
| Slag | Regular fuel | 2.9–11.1 | 0.2–0.5 | 0.02–0.6 |
| | 4.5% MBM test | 6 | 0.55 | 0.06 |

**Table 12**
Summary of the references in which the influence of several gasification variables on important gasification issues are studied.

| On\Influence of | Bed reactor T | Secondary bed reactor T | Equivalence ratio | Secondary bed height | %MBM | Air flow rate | dp |
|---|---|---|---|---|---|---|---|
| Product yields | [21] | [21] | [21] | [21] | | | |
| Gas composition | [2,21] | [21] | [21] | | [15] | | |
| Gas heating value | [2,21] | [21] | [21] | [21] | | [22] | [22] |
| Char composition | [2] | | | | [15] | | |

dp = particulate size.

**Table 13**
Comparison of product yields in pyrolysis and gasification processes.

| Process | Authors | Liquid yield (wt.%) | Gas yield (wt.%) | Solid yield (wt.%) | Gas heating value | Energetic yield |
|---|---|---|---|---|---|---|
| Pyrolysis | Chaala and Roy [4] | 48.7 | 9.4 | 39.1 | 12.9 MJ/kg | |
| | Ayllón et al. [25] | 55 | 10 | 35 | 16 MJ/m$^3$ | 0.12 |
| Gasification | Fedorowicz et al. [2] | | | 27 | 14.9 MJ/m$^3$ | |
| | Soni et al. [21] | 22.9 | 22.1 | 47 | 16 MJ/m$^3$ | |
| | Priyadarsan et al. [22] | | | | 4.5–5.12 MJ/kg | |

**Table 14**
Summary of references.

| Authors | Process | Feeder system | Operational conditions | Products analysed | Results |
|---|---|---|---|---|---|
| Fryda et al. [13] | Co-combustion in a fluidised bed reactor | Continuously by means of a screw feeder | Air as gasification gas<br>3 kg of silica sand inside the fluidised bed<br>MBM/coal blends (10–20% MBM/90–80% coal) | CO, $SO_2$, $NO_x$, $N_2O$ emissions<br>Agglomeration tendencies<br>Bed material characterisation | Introducing MBM in the coal combustion process causes CO and $NO_x$ increase and reduces $N_2O$ and $SO_2$ emissions<br>Introducing MBM avoids severe agglomerations in the bed reactor |
| Fryda et al. [14] | Co-combustion in a fluidised bed reactor | Continuously by means of a screw feeder | Air as gasification gas<br>3 kg of silica sand inside the fluidised bed<br>MBM/coal and MBM/olive bagasse blends | CO, $SO_2$, $NO_x$, $N_2O$ emissions<br>Agglomeration tendencies<br>Bed material characterisation | Introducing MBM in the coal combustion process causes CO and $NO_x$ increase and reduces $N_2O$ and $SO_2$ emissions<br>Introducing MBM avoids severe agglomerations in the bed reactor |
| Gulyurtlu et al. [16] | Co-combustion in a fluidised bed reactor | Continuously by means of a screw feeder | MBM/coal blends (20% and 50% of MBM)<br>Temperatures between 730 and 850 °C | Gas parameters<br>Gas emissions<br>Ash characterisation<br>Bed agglomeration | The addition of MBM in coal combustion processes does not affect the $NO_x$, $N_2O$, VOCs, $SO_2$ emissions<br>MBM co-combustion produces more fly ashes than coal combustion |
| Miller et al. [20] | Co-combustion in a circulating fluidised bed reactor | Continuous | Sand bed<br>Flue gas recirculation<br>MBM/coal blends (from 10% to 22% MBM)<br>Temperatures from 1200 to 1700 °F | CO, $CO_2$, $SO_2$ and $NO_x$ emissions | The feed location and temperature have an important effect on CO emissions<br>Flue gas recirculation did not have a significant effect on CO emissions<br>The addition of MBM in coal combustion processes decreases $SO_2$ emissions |
| McDonnell et al. [34] | Co-combustion in a fluidised bed reactor | Continuously with screw feeder | Sand bed<br>Temperatures of 820 and 880 °C<br>MBM/peat blends (15–35% MBM)<br>100% MBM | Ash composition<br>CO, $CO_2$, $SO_2$, $NO_x$, VOCs, PDB, PCDD and PCDFs emissions | Bled agglomeration occurs with 35% MBM blends at 880 °C temperature<br>To introduce MBM in the coal combustion process causes CO to increase and reduces NO emissions |
| Heikkinen et al. [29] | Co-combustion in an electrically heated pulverized fuel reactor | Continuously with a screw feeder | Temperature = 1300 °C<br>20% MBM–80% coal blend | CO, $CO_2$ and $O_2$ flue gas | Development of a co-combustion model<br>Application of the model to MBM and coal co-combustion |
| Beck et al. [10] | Co-combustion | | Temperatures between 400 and 1400 °C | | Mechanism of catalyst deactivation in the co-combustion process |
| McDonnell et al. [18] | Co-combustion in a fluidised bed reactor | Semi-continuously via pneumatic injection | 1.2 g MBM/peat pelletized blends (0–100% MBM)<br>Temperature = 800 °C | | The residence time decreases when %MBM in the blend increases |
| Lopes et al. [33] | Co-combustion in a fluidised bed reactor | Continuously with a screw feeder to the top of the bed | MBM/coal blends (5, 15,25 and 100 wt.% of MBM)<br>Excess of air between 30–40%<br>Temp. 700–800 °C | Particulate matter emissions (PM)<br>PCDD/F emissions | PM emissions increase when MBM combustion is carried out<br>PCDD/F emissions ranged from 6% produced in coal combustion to 97.3% in MBM combustion |
| Coutand et al. [7] | Co-combustion in electrical furnace | Non-continuous | 95 wt.% MBM–5 wt.% other waste (plastic bags or sewage sludge)<br>First combustion at 600 °C and second combustion at temperatures between 25 and 800 °C<br>Heating rate = 2 °C/min | Ash composition and characterisation | MBM bottom ashes from combustion processes can be classified as inert waste and to be land-filled<br>MBM fly ash needs stabilization or washing treatment to be land-filled |
| Cummins et al. [12] | Co-combustion in a fluidised bed reactor | Continuously with a screw feeder to the top of the bed | 20 wt.% MBM–80 wt.% peat mixture<br>Temperatures 880–885 °C | $NO_2$, CO, HCl, $SO_2$, $PM_{10}$ emissions | It is possible to burn MBM with peat without exceeding the emission standards set out in international laws |

Table 14 (*Continued*)

| Authors | Process | Feeder system | Operational conditions | Products analysed | Results |
|---|---|---|---|---|---|
| Gulyurtlu et al. [41] | Co-combustion in a fluidised bed reactor | Continuously by means of a screw feeder | MBM/coal mixture (5, 15, 25 and 100 wt.% of MBM)<br>Temperatures 800–830 °C | Dioxins emissions<br>Ashes characterisation | Chlorine emissions increased when MBM was added<br>Co-combustion of MBM with coal may increase the PCDD/F formation |
| Essien Etok et al. [40] | Combustion in an electrical furnace | Non-continuous | 50 g MBM<br>Temperatures 400–900 °C<br>Heating rate of 30 °C/min | | Structural and chemical changes in thermal treatment of bones |
| Deydier et al. [36] | Combustion in thermobalance | Non-continuous | Temperatures between 550 and 1000 °C<br>Heating rate = 3 °C/min | Ash composition and characterisation | Thermal conditions of MBM combustion induce a wide range of ash structural modifications. A strong decrease in the particle surface area (from 18 to 2 $m^2$/g) in the ashes was described |
| Coutand et al. [44] | Combustion in electrical furnace | Non-continuous | First combustion at 600 °C and second combustion at temperatures between 25 and 800 °C<br>Heating rate = 2 °C/min | Ash composition and characterisation | Kinetic and mechanistic studies of MBM ashes as cadmium immobilizing material<br>The results show the efficiency of MBM combustion residue for removing cadmium from contaminated aqueous solutions |
| Deydier et al. [42] | Combustion in electrical furnace | Non-continuous | Temperatures until 850 °C<br>Heating rate = 2 °C/min | Ashes characterisation | Kinetic of lead removal by MBM ashes |
| Deydier et al. [43] | Combustion in electrical furnace | Non-continuous | Temperatures until 800 °C<br>Heating rate = 2 °C/min | Ashes composition | Mechanism of lead removal in polluted aqueous solutions by MBM ashes |
| Paisley and Hostrup-Pedersen [6] | Combustion in a gas-fired power plant | | | | Estimation of BSE infectivity by means of simulation models<br>The risk of using MBM combustion ashes as fertilizer is negligible |
| Conesa et al. [5] | Pyrolysis and combustion in thermobalance | Non-continuous | Heating rate of 10,20 and 30 K/min<br>Temp. 80–800 °C | | A kinetic model to describe MBM thermal decomposition was developed |
| Senneca [19] | Pyrolysis, gasification and combustion in thermobalance<br>Co-combustion of MBM with coal | Non-continuous | Gasification with CO2<br>6% MBM–94% Coal | Ash characterisation<br>Ash composition<br>Activation energy of char | Kinetic model of MBM thermal decomposition<br>Comparison between ash from coal combustion and ash from MBM/coal co-combustion |
| Conesa et al. [11] | Pyrolysis and combustion in a thermobalance | Non-continuous | 0.1 g of MBM<br>Temperatures 600–1100 °C<br>Heating rate of 5, 20, 50, 100 °C/min | Dioxin and furans production | Dioxins and furans produced in a MBM combustion process are higher than produced in MBM pyrolysis process. However dioxins produced at 850 °C are higher in pyrolysis than in combustion, and furans produced at 1100 °C are higher in pyrolysis processes |
| Conesa et al. [24] | Pyrolysis and combustion in a thermobalance | Non-continuous | 0.1–0.2 g of MBM<br>Temperatures 450–1050 °C | Dioxin and furans production | The formation of PCDD/Fs is important in both combustion and pyrolysis processes<br>PCDD/Fs level in MBM combustion is similar to the emissions of other wastes combustion<br>In a pyrolysis process at 850 °C, high emission factor of PAHs (polyaromatic hydrocarbons) can be produced<br>In a combustion process at 850 °C, methane, benzene and PAHs production are important |

Table 14 (*Continued*)

| Authors | Process | Feeder system | Operational conditions | Products analysed | Results |
|---|---|---|---|---|---|
| Skodras et al. [17] | Pyrolysis and combustion in thermobalance | Non-continuous | 20 mg of MBM<br>Temperatures 300–1000 °C<br>Heating rate of 20 °C/min | | MBM thermal decomposition was studied<br>MBM has good fuel properties to be used in boilers as a secondary fuel<br>Operational problems could arise due to the high phosphorous, calcium and chloride in MBM |
| Ayllón et al. [25] | Pyrolysis in a fixed bed reactor | Non-continuous | Temperature300–900 °C<br>30 g of MBM sample<br>13 $cm^3$/s of $N_2$ flow<br>Heating rate: 2–14 °C/min<br>Gas residence time 3.31–4.60 s | Product yields<br>Gas composition<br>Gas heating value<br>Tar composition<br>Char composition | The optimum temperature for obtaining the maximum tar production at 450 °C<br>The gas yield increases when temperature increases<br>Gas heating value is highest at 650 °C |
| Chaala and Roy [4] | Vacuum pyrolysis in a fixed bed reactor | Non-continuous | 516.5 g of pelletized MBM<br>Temperature = 500 °C<br>Heating rate = 15 °C/min | Product yields<br>Tar composition<br>Aqueous phase composition<br>Gas composition<br>Char composition | The oil produced (High heating value = 34.2 MJ/kg) can be used as a fuel in boilers<br>The gas (heating value = 12.9 MJ/kg) and the aqueous phase can be co-fired to provide heat to the process<br>The solid residue can be used as a fertilizer or as solid fuel in cement kilns |
| Ayllón et al. [8] | Pyrolysis in thermobalance | Non-continuous | 10, 15 and 20 mg of MBM<br>$N_2$ flow rates of 80 and 130 $cm^3$/min<br>Heating rate of 20 °C/min<br>Temper. 0–900 °C | | A kinetic model to describe MBM thermal decomposition was developed |
| Skodras et al. [35] | Pyrolysis in thermobalance | Non-continuous | Temperatures 300–1000 °C<br>Heating rate of 5, 20, 50, 100 °C/min | | A kinetic model to describe MBM thermal decomposition was developed |
| Fedorowicz et al. [2] | Gasification in a fluidised bed reactor | Non-continuous<br>From the top of the reactor/brass plunger with a ball valve | Temperature = 1000 °C<br>9 g of MBM frozen<br>Sand bed<br>Gas carrier: $N_2$ and steam | Gas yield<br>Gas composition<br>Gas heating value | MBM was successfully fed into the gasification system<br>Energy density of 400 Btu/$ft^3$ ($N_2$ free basis) MBM was produced |
| Soni et al. [21] | Gasification in a fixed bed reactor and gasification in a two-stage fixed bed reactor system | Non-continuous | Temperature 650–850 °C<br>2 g of MBM<br>Heating rate = 25 °C/min | Product yields<br>Gas composition<br>Gas heating value | Gas yield and gas heating value, increase with temperature whereas char and tar yields decrease<br>Gas yield increases with the equivalence ratio, whereas gas heating value, char and tar yields decrease<br>CO and $CO_2$ increase and decrease with temperature respectively |
| García-Peña et al. [15] | Co-gasification of MBM–coal and petroleum coke (fuel) in IGCC plant (gasifier pressure = 25 bar) | Continuously by pneumatic pump<br>Pressurized | Temperatures up to 1600 °C<br>28.5 kg/s of solid feed<br>Gas: oxygen and steam | Gas composition<br>Steam/coal ratio and $O_2$/coal ratio<br>Ash compost<br>Water analysis<br>Operational cost | There is no appreciable effect of adding MBM on the results obtained in usual fuel gasification<br>No effect of MBM as fusion agent was observed |
| Priyadarsan et al. [22] | Coal co-gasification with chicken litter biomass in a fixed bed 10 kWt reactor | Non-continuously from the top by gravity | Temperature = 1000 K<br>4–5 kg of sample | Gas composition<br>Gas heating value | The airflow rate and the fuel particulate size do not affect the gas composition |
| Ro et al. [23] | Catalytic wet gasification of animal wastes | | 350 °C catalysis | Gas composition | Wet gasification reactions |

systems have not yet been tested with MBM. There is therefore an important need to enhance our knowledge of MBM pyrolysis and gasification processes. The evaluation of the influence of different variables on important process parameters is essential in order to valorise both processes as potential alternatives for managing MBM wastes.

Furthermore, the liquid produced in gasification and co-gasification of MBM has not been analysed to date. It is important

to study the composition of this liquid fraction in order to find potential environmentally friendly uses for it.

As regards MBM combustion, certain aspects remain to be analysed. For example, the solid waste produced in MBM combustion has a CaO high content that could reduce $NO_x$ and $N_2O$ emissions due to its catalyst effect [14]. For this reason, the effect of replacing the sand bed in fluidised bed combustors by char from MBM combustion in thermal processes should be analysed as a possible use for this residue.

## 5. Summary and conclusions

This literature review demonstrates that the thermal treatment of MBM by means of pyrolysis, combustion and gasification has been studied in different types of reactors including thermobalance units, fluidised bed reactors and fixed bed reactors. The most extensively analysed treatment is co-combustion with coal, the results of which are promising from the point of view of managing this type of residue. However, more research into MBM pyrolysis and gasification is required in order to assess their suitability as real alternatives for treating MBM waste.

Some feeding problems due to stickiness have frequently been described as a consequence of the high fat content in MBM [14,20,29], thus co-treatments with coal and peat have been broadly analysed.

The products obtained from these processes have been studied in order to find potential uses for them. The ashes produced in combustion and co-combustion of MBM has been demonstrated to be potential fertilizer due to their high phosphorous content [7,42]. This solid waste is also a possible pollutant removal of hazardous metals in aqueous effluents [6,42–44]. The emissions of VOCs, PCDD/Fs, $SO_2$, $NO_x$ and CO have also been evaluated [13,14,16,20,33,34,41]. Although $N_2O$ and $SO_2$ emissions decrease when a low percentage of coal is substituted by MBM, CO and $NO_x$ emissions increase with the increasing quantity of MBM. However, the levels of these emissions are well within the limits established by international regulations.

MBM pyrolysis has only been evaluated in bench scale plants while MBM–coal co-gasification has also been tested in a commercial plant [15]. In general, all the studies have determined the product yields at different operational conditions for these processes. Table 13 summaries the product yields obtained in MBM pyrolysis and gasification treatments.

Potential applications of pyrolysis char include its use as a fertilizer, due to its high NPK content [4]. Its high compressive strength and low water absorption capacity suggest it could be a possible aggregate for the manufacture of concrete [4].

The pyrolysis liquid composition has been analysed by means of GC–MS [4,25] and GC-FID [25]. Nitrogenated aliphatic compounds are the most abundant in any temperature range (reaching about 83% of the tar production at 500–550 °C). However, the liquid product from MBM gasification and co-gasification processes has not yet been analysed.

The compounds analysed in the pyrolysis and gasification gas product (in a nitrogen free basis) are $CO_2$, CO, $CH_4$, $H_2$, $C_2H_4$, $C_2H_6$, $C_2H_2$ and $H_2S$ [2,25]. Due to its low nitrogen content and its heating value, the pyrolysis gas could be co-fired to provide heat for thermal process [4]. The gas product obtained from the gasification processes contains combustibles that make it a potential candidate for energy production [2]. Furthermore, a comparison among PCDD/Fs produced in the pyrolysis of MBM and other pyrolysis wastes show that the total PCDD/Fs produced in MBM pyrolysis are 10 and 20 times less than the amounts produced in the pyrolysis of sewage sludge and PVC, respectively.

Table 14 provides a schematic summary of the main published works concerning thermochemical treatments involving MBM. The process evaluated including the feeder system used in each work is indicated. The operational conditions and the products analysed are also displayed. Finally, a brief summary of the main results obtained in each study is included.

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